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APPLICATION NUMBER: ***60/543,104***
FILING DATE: ***February 09, 2004***
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a requ st for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Nathalie	**Leroux**	**16 Impasse du Verger, 33500 Libourne, France**

☐ *Additional inventors are being named on the ____ separately numbered sheets attached hereto*

15535 U.S. PTO
60/543104
020904

TITLE OF THE INVENTION (280 characters max)

Reversible Thermochromic Systems from Colorless to Color

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

☐ Customer Number **000025900** → *Place Customer Number Bar Code Label here*

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☒ Firm *or* Individual Name	**Sun Chemical Corporation**				
Address	**222 Bridge Plaza South**				
Address					
City	**Fort Lee**	State	**NJ**	ZIP	**07024**
Country		Telephone		Fax	

ENCLOSED APPLICATION PARTS ***(check all that apply)***

☒ Specification *Number of Pages* **4**

☐ CD(s), Number

☐ Drawing(s) *Number of Sheets*

☐ Other (specify)

☐ Application Data Sheet. See 37 CFR 1.76

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: ______

Respectfully submitted,

SIGNATURE Sidney Persley

Date **02/06/04**

TYPED or PRINTED NAME **Sidney Persley**

REGISTRATION NO. *(if appropriate)* **34,898**

Docket Number: **C-611**

TELEPHONE **201-224-4600 Ext. 278**

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10) Applicant(s): **N. Leroux**			Docket No. **C-611**
Serial No.	Filing Date	Examiner	Group Art Unit

Invention: **Reversible thermochromic systems from colorless to color**

I hereby certify that the following correspondence:

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PROVISIONAL PATENT APPLICATION INVENTION RECORD

Sun Chemical Corporation

Inventor(s)	Case #	Origin
Nathalie Leroux	C-611	AIC

Descriptive Title
Reversible thermochromic systems from colorless to color

Status of Invention	
Conception Date	**Date of 1st use or Sale**

Brief Abstract of Invention
The object of this invention is to develop reversible thermochromic systems which go from a colorless state to colored state as the temperature is increased. These systems are two components systems based on an electron donating dye (color former) and an electron accepting compound (developer). A preferred electron accepting compound is a low acidic compound: an long chain aliphatic carboxylic acid which melting point is the trigger of the color's apparition. A preferred color former is a phthalide derivative. The temperature of the color apparition is the melting point of the developer and the temperature of the color disparition is its recrystallization temperature.

1st Written Description Date:	Where Recorded:	Date Prepared:	Date Received:	Rating:

BACKGROUND OF INVENTION

The major application for thermochromic systems which go from a colorless state to colored state as the temperature is increased is for rewritable printing material. Among published patents, there are several proposals of using various kinds of bistable thermochromic compositions developed for rewritable systems. A number of compounds have been identified that may be reversibly colored upon application of heat energy, and which are bistable. Once placed into one or the other state (e.g. colorless or colored), the substance exhibits hysteresis, tending to persist in that state under ordinary ambient conditions. Based on their imaging function, these compounds can be divided into:
1.The systems that are both writable and erasable through heating to different temperatures or with different heat cycles; 2.The systems that require heating and cooling to write and erase; and 3.The systems that require heat and an electrical field to write and erase. Bistable thermochromic compositions, based on their mechanism and principle of operation can be classified into the following three main categories of polymer organic crystal, color-formers /developers /erasers systems, and smectic liquid crystal systems. Polymer organic crystal composite are based on crystal size variation of a low molecular organic compound dispersed in the polymer matrix depending on thermal changes. The variation is between large single crystalline state that is transparent allowing light transmission and polycrystalline state that is turbid causing light scattering. Therefore the material can be repeatedly switched between transparent and opaque states depending on heating to different temperatures. Color-formers /developers /erasers systems compositions consist of three main components: a coloring agent (e.g. from the group of leuco dyes, lactone dyes, etc.), a developing/tone-reducing agent (e.g. from the group of urea, phosphoric acid, aliphatic carboxylic, phenolic compounds, etc.) and a matrix or binder resin (e.g. steroid, etc.). Reversible coloring and decoloring of the composition is achieved by exposing the system to different thermal energy levels causing coloring agent and developing/tone-reducing agent to react (development) forming a colored state or to separate (tone reduction) forming a decolored state. The smectic mesomorphic thermochromic system is based on smectic liquid crystals due to their bistability during phase change between opaque and transparent states.

PRIOR ART

Polymer/Organic Crystal Composites

US 4268413 (1981) : Polymer-organic crystal system, before being employed for imaging applications, was initially developed and proposed for use in temperature-measuring devices, temperature indicating devices, smart windows for protection against solar radiation, etc. **US 4734359 (1988), 5158924 (1992), 5278129 (1994), 5298476, 5306689, 5521371, 5556827, 5627126, 5780387 (1998) and 5948727 (1999) :**Polymer-organic crystal thermochromic composition (also known as low molecularweight system or transparent/opaque type) is made of a polymer/resin matrix (e.g. polyvinylacetal, polystyrene/polybutadiene copolymer, polyvinylacetate, vinylchloride/vinylacetate copolymer, etc.) and an organic low-molecular weight substance (fatty acids such as stearic acid, behenic acid, etc.) dispersed therein .

Dyes complex systems

US 5178669 (1993), 5274460 (1993), 5296439, 5395433, 5432534, 5534685, 5552364, 5583088, 5585320, 5641724, 5663115, 5679615, 5702850, 5710094, 5721059, 5849651, 5869420, 6001518 (1999), 6004899 (1999) and 6010808 (2000): Various kinds of dye complex thermochromic compositions (also known as coloring/decoloring type) have been proposed in these patents: **US 5178669 (1993) and 5274460 (1993) :** These inventions described the first category where systems include a leuco dye and a developing/tonereducing agent adapted to thermally interact with the dye and a suitable binder. Exposure of the system to a first thermal energy level (e.g. heating to a high temperature of 200-350°C for a short duration of 1-3 msec) produces a color, while exposure to a second thermal energy level (e.g. heating to a low temperature of 80- 150°C for a longer duration of 5msec to 2 sec) renders the system transparent. The developing/tone reducing agent is a substance having, in the same molecule, a group that exhibits a thermally triggered color-developing property with respect to the leuco dye, and a group that exhibits a thermally triggered tone-reducing property with respect to the leuco dye. The agent may be a salt of a phenolic carboxylic acid and an organic amine, which can be thermally induced to behave as an acid or a base. To state more specifically, the color developing and reducing agent is an amphoteric compound and, under the action of heat, it exhibits the nature of either an acid or a base to work either as a color developing agent or as a color reducing agent with respect to the leuco compound. Under acidic conditions, the lactone rings of the leuco dye open and the molecule becomes colored; exposure to basic conditions closes the rings and restores the original colorless state. The temperatures of the color change are quiet different one from each other (200-350 °C for the colo development and 80 to 150 °C for the erasure).

US 5470816 (1995):Other examples of the first category include systems using dimerized or trimerized urea developers. **US 5432534 (1995)** :Other examples of the first including a thermally sensitive coloring agent such as a triphenylmethane phthalide compound, a fluoran compound, a phenothiazine compound, a leuco auramine compound or an indolinophthalide compound, and a color developer such as a phosphoric acid compound, an aliphatic carboxylic compound or a phenolic compound. **US 5480482 (1996)** :An example of the second category is a reversible thermochromic pigment including a mixture of a colorless cyclic aryl lactone dye that undergoes ring opening to form a colored triaryl-methylene carboxylic acid dye, an alkaline (diaminoalkane) activator agent that effects ring opening of the dye when the mixture is heated and ring closure to the colorless lactone state when the mixture is cooled, and a low-melting solid that functions as a solvent and activator. Generally, the dye is rendered colorless through heating to temperatures of 30-70°C, and colored through cooling to temperatures below 25°C. Thus, the mechanism is analogous to that described earlier (US 5178669 and 5274460. No applications in any resin or polymer are given. It is just a PH indicator and basic component reaction description. **US 553907 (1996)**: Reversible thermosensitive coloring recording method, recording medium and recording apparatus for the recording method. **US 5552364 (1996) and 5585320 (1996)** : These patents described the development of multi-color images: one method suggests using plurality of the thermochromic coloring composition layers, which are successively overlaid one on top of the other, each of them being independently present separated from the other layers. Intermediate layers made of a resin are interposed between the coloring composition layers preventing them from being fused and bonded to each other. Each of the coloring composition layers forms a colored state with a different color and a decolorized state in a predetermined

temperature ranges. Therefore, when heat is applied at a temperature at which all of the coloring composition layers develop their respective colored states, the recording medium forms a mixed coloring state. When heat is further applied to the same mixed coloring state at a specific decolorizing temperature that its range being located lower than the development temperature range, the mixed colored image is decolorized or a single color image is formed. By repeating such operation, a single colored image or a mixed colored image can be obtained as desired. **US 6022648 (2000) :** Massachusetts Institute of Technology, Cambridge, Mass., well known with her invention of electronic ink, also hands-on in bistable thermochromic systems, discloses methods of incorporating thermochromic materials into constructions producing full-color images and multiple gray levels.

Smectic Liquid Crystal Systems

US 5847786 (1988), 5851422, 6052137, 6059993 (2000) and 6201587 (2001) : Reversible imaging media are obtained when a smectic liquid crystal is dispersed in a polymer matrix creating the so-called polymer dispersed liquid crystal film (PDLC film).

SUMMARY OF INVENTION

The invention is the development of reversible thermochromic systems which go from a colorless state to colored state as the temperature is increased. The systems are two components systems based on an electron donating dye (color former) and an electron accepting compound (developer). The system exhibits two different colored states depending on the temperature and goes from a colorless state to colored state as the temperature is increased.

ADVANTAGES OVER PRIOR ART

The system is only a two components systems whose color is temperature dependant. The thermochromic effect is from colorless to color as the temperature is increased and from color to colorless as the temperature is decreased. The system is a two component system based on an electron donating dye (color former) and an electron accepting compound (developer) and could be incorporated in tri-dimensional matrix such as an ink.

DESCRIPTION OF INVENTION

The color change system developed in this invention is a bi components system having a color former and a developer. A preferred electron accepting compound (developer) is a low acidic compound : an long chain aliphatic carboxylic acid which melting point is the trigger of the color's apparition. The preferred color former is a phthalide derivative. The temperature of the color apparition is the melting point of the developer and the temperature of the color disparition is its recrystallization temperature. At low temperature, the colorless system is stabilized by chain interactions between the aliphatic tails and hydrogen bonds between the oxygen and alcohol groups, and the color former is in its colorless state and once the melting point of the developer is reached, the aliphatic chains set the system free, sufficient energy is reached and the acidic effect of the carboxylic acid can achieve the coloration of the leuco dye. The ratio of each component (ionochronic compound / developer system) may vary according to the required contrast and colored change. All the components are mixed together at room temperature. The temperature of the color change is depending on the melting temperature of the developer and a large range of temperature can be achieved in varying the length of the chain of the aliphatic acid. The colorations which can be obtained are depending on the ionochronic dyes and their intrinsic coloration. All the range of color can be achieved. The color change can be

from a colorless state to a color state or from a color to another color state using a pigment in the mixture. As example, by using a blue pigment in the system plus a magenta color-former, a blue to violet system can be achieved.
A preferred color former is the 3,3-bis(1-n-butyl-2-methyl-indol-3-yl)phthalide (called red 40 from Yamamoto chemical). When used with the developer dodecanoic acid, the final reversible system go from a colorless state to a colored one when the temperature reached the melting point of the dodecanoic acid, i.-e. around 46 °C.
The system is mixed with an ink vehicle which would not react neither with the color former nor the developer system. The ink vehicle is choosen versus the application.